



OFFICE OF NAVAL RESEARCH
Grant No. N00014-90-J-1263
RCT Project 4133002---05
Technical Report #20

PHASE TRANSITIONS AT THE FLUID-SOLID INTERFACE IN A
MODEL FOR THE ADSORPTION OF HARD SPHERES

by

Dale A. Huckaby* and L. Blum**

Prepared for Publication in the
Condensed Matter Physics, Vol. 8, Blum, L. and
Malik, B., Editors, Plenum Press, New York, 8 (1993)

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*Department of Chemistry, Texas Christian University
Fort Worth, Texas 76129, USA

and

**Department of Physics, University of Puerto Rico
P.O. Box 23343
Rio Piedras, P.R. 00931-3343, USA

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REPORT DOCUMENTATION PAGE

1a REPORT SECURITY CLASSIFICATION		1b RESTRICTIVE MARKINGS	
2a SECURITY CLASSIFICATION AUTHORITY		3 DISTRIBUTION AVAILABILITY OF REPORT	
2b DECLASSIFICATION/DOWNGRADING SCHEDULE			
4 PERFORMING ORGANIZATION REPORT NUMBER(S) Technical Report #20		5 MONITORING ORGANIZATION REPORT NUMBER(S)	
6a NAME OF PERFORMING ORGANIZATION Physics Department University of Puerto Rico	6b OFFICE SYMBOL (If applicable)	7a NAME OF MONITORING ORGANIZATION	
6c ADDRESS (City, State, and ZIP Code) Río Piedras Puerto Rico 00931-3343		7b ADDRESS (City, State, and ZIP Code)	
8a NAME OF FUNDING/SPONSORING ORGANIZATION Chemistry Office of Naval Research	8b OFFICE SYMBOL (If applicable) Code 472	9 PROCUREMENT INSTRUMENT IDENTIFICATION NUMBER RCT Project 4133002---05	
8c ADDRESS (City, State, and ZIP Code) Arlington Virginia 22217-5000		10 SOURCE OF FUNDING NUMBERS	
		PROGRAM ELEMENT NO	PROJECT NO
11 TITLE (Include Security Classification) Phase Transitions at the Fluid-Solid Interface in a Model for the Adsorption of Hard Spheres			
12 PERSONAL AUTHOR(S) D.A. Huckaby and L. Blum			
13a TYPE OF REPORT Paper	13b TIME COVERED FROM TO	14 DATE OF REPORT (Year, Month, Day) 1-15-93	15 PAGE COUNT 11
16 SUPPLEMENTARY NOTATION			
17 COSATI CODES		18 SUBJECT TERMS (Continue on reverse if necessary and identify by block number)	
FIELD	GROUP SUB-GROUP		
19 ABSTRACT (Continue on reverse if necessary and identify by block number) Phase transitions at the fluid-solid interface are studied using an adsorption model consisting of a fluid of hard spheres in contact with a planar wall which contains a lattice of sticky adsorption sites. The model is equivalent to a lattice gas with n-body interactions that are related to the n-body correlation functions of the fluid.			
20 DISTRIBUTION/AVAILABILITY OF ABSTRACT <input type="checkbox"/> UNCLASSIFIED/UNLIMITED <input type="checkbox"/> SAME AS RPT <input type="checkbox"/> DTIC USERS		21 ABSTRACT SECURITY CLASSIFICATION	
22a NAME OF RESPONSIBLE INDIVIDUAL Dr. Robert Nowak		22b TELEPHONE (Include Area Code) (203) 696-4410	22c OFFICE SYMBOL ONR 472

PHASE TRANSITIONS AT THE FLUID-SOLID INTERFACE IN A MODEL FOR THE ADSORPTION OF HARD SPHERES

Dale A. Huckaby¹ and Lesser Blum²

¹Department of Chemistry, Texas Christian University
Fort Worth, Texas 76129

²Department of Physics, University of Puerto Rico
Rio Piedras, Puerto Rico 00931-3343

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Phase transitions at the fluid-solid interface are studied using an adsorption model consisting of a fluid of hard spheres in contact with a planar wall which contains a lattice of sticky adsorption sites. The model is equivalent to a lattice gas with n-body interactions that are related to the n-body correlation functions of the fluid.

I. INTRODUCTION

The present paper is an overview of some of the results we have obtained in the past three years using a statistical mechanical model to study phase transitions which occur at the fluid-solid interface.¹⁻³ The model,^{4,5} as discussed in Sec. II, consists of a dense fluid of hard spheres of diameter σ near a planar wall that contains a triangular lattice of sticky sites. This three-dimensional model is equivalent to a two-dimensional lattice gas with many-body interactions that are related to the many-body contact correlation functions of the fluid.

The nature of the phases which occur at the fluid-solid interface in this model depends on the fluid density, the strength of the sticky attraction at the lattice sites, and also on the ratio of the hard sphere diameter to the lattice spacing d . If σ slightly exceeds d , if the pair correlation functions are assumed to be unity at distances exceeding d , and if many-body correlation functions are approximated using the Kirkwood superposition approximation,⁶ the adsorption model is then equivalent to the hard-hexagon lattice gas solved by Baxter.⁷ The isotherms for this case of the adsorption model, which undergoes an order-disorder phase transition, can be calculated using some exact

expressions obtained by Joyce⁸ for the hard-hexagon model. These results are presented in Sec. III along with some simplified expressions for the isotherms which we obtained by exploiting a symmetry present in Joyce's original expressions.

If the sphere diameter σ is much smaller than the lattice spacing d , so that the correlation functions are approximately unity at distances as large as d , then the model has no phase transition and the Langmuir adsorption isotherm results.²

We have treated in some detail the special case for which $\sigma = d$.¹⁻³ Simple, but accurate analytical expressions are known for the contact pair correlation function as a function of the fluid density.⁹⁻¹¹ Assuming the pair correlation functions decay to approximately unity at distances approaching the second neighbor lattice spacing, and using the Kirkwood superposition approximation, the adsorption model is equivalent to a lattice gas with first-neighbor pairwise interactions.^{1,5} The coexistence surface for the first-order phase separation which occurs in this lattice gas is known exactly.¹² Using several exactly known coefficients in the series expansion of the properties of the lattice gas,¹³ we obtained accurate adsorption isotherms which are a generalization of Langmuir's isotherm.² These results are presented in Sec. IV.

Recent calculations by Attard and Stell indicate that the Kirkwood superposition approximation is not accurate for a triangle of hard spheres all in mutual contact.^{14,15} Since such a configuration is present in the adsorption model if $\sigma = d$, we have included the effects of three-body interactions in this case of the model. The critical point of the equivalent lattice gas, which contains pair and triplet interactions, has been approximated¹⁶ using the interface method of Müller-Hartmann and Zittarz.¹⁷ In addition, we discovered a simple but accurate analytical approximation to the three-body correlation function for three spheres in mutual contact.³ Together these results yielded an estimate of the fluid density at the critical point of the two-phase coexistence surface for the adsorption model³ which is significantly higher than that predicted using only the contact pair correlation function and the Kirkwood superposition approximation.¹ These results are presented in Sec. V.

II. THE MODEL

We consider a model for adsorption in which a fluid of N hard spheres of diameter σ in a volume V interacts with a hard wall, located at $z = -\sigma/2$, containing a lattice Λ of sticky adsorption sites.^{1,4,5} The partition function for the system is

$$Z = \frac{1}{N!} \int e^{-\beta H} d\mathbf{r}^N, \quad (1)$$

where $\beta = (kT)^{-1}$. The Hamiltonian can be written as

$$H = H_0 + \sum_{i=1}^N U^s(\mathbf{r}_i), \quad (2)$$

where H_0 is the Hamiltonian for the system in the absence of the sticky sites (the smooth wall problem), and $U^s(\mathbf{r}_i)$ is the potential for the interaction of a hard sphere i at \mathbf{r}_i with the lattice of sticky sites $\{\mathbf{R}_s\}$. This sticky potential can be written as

$$e^{-\beta U^s(\mathbf{r}_i)} = 1 + \lambda \sum_{\mathbf{R}_s \in \Lambda} \delta(\mathbf{r}_i - \mathbf{R}_s), \quad (3)$$

where δ is the Dirac delta function. The stickiness parameter λ has units of volume and, except for a constant factor, is the fugacity of adsorption of a hard sphere onto a sticky site.

Performing the integrations in Eq. (1) to remove the delta functions and rearranging terms yields

$$Z/Z_0 = \sum_{n=0}^N \frac{\lambda^n}{n!} \sum_{\{\mathbf{R}_i\} \subset \Lambda} \rho_n^0(\mathbf{R}_1, \dots, \mathbf{R}_n), \quad (4)$$

where

$$\begin{aligned} \rho_n^0(\mathbf{r}_1, \dots, \mathbf{r}_n) &= [Z_0(N-n)!]^{-1} \int e^{-\beta H_0} d\mathbf{r}_{n+1} \dots d\mathbf{r}_N \\ &= g_n^0(\mathbf{r}_1, \dots, \mathbf{r}_n) \prod_{i=1}^n \rho_1^0(\mathbf{r}_i). \end{aligned} \quad (5)$$

Here, Z_0 , $g_n^0(\mathbf{r}_1, \dots, \mathbf{r}_n)$, and $\rho_1^0(\mathbf{r}_i)$ are respectively the partition function, an n -body correlation function, and the single particle density for the smooth wall problem.

Defining the potential of mean force $U(\mathbf{R}_1, \dots, \mathbf{R}_n)$ as

$$g_n^0(\mathbf{R}_1, \dots, \mathbf{R}_n) = e^{-\beta U(\mathbf{R}_1, \dots, \mathbf{R}_n)} \quad (6)$$

yields

$$Z/Z_0 = \sum_{n=0}^N \frac{[\lambda \rho_1^0(0)]^n}{n!} \sum_{\{\mathbf{R}_i\} \subset \Lambda} e^{-\beta U(\mathbf{R}_1, \dots, \mathbf{R}_n)}, \quad (7)$$

where $\rho_1^0(0)$ is the single particle density at the contact plane ($z = 0$). Changing from a sum over the positions of labelled hard spheres on Λ to a sum over lattice sites of Λ , Eq. (7) yields

$$\Xi = Z/Z_0 = \sum_{\{t_i\}} [\lambda \rho_1^0(0)]^{\sum t_i} e^{-\beta U(\{t_i\})} , \quad (8)$$

where t_i is the occupation number of site i in a given configuration $\{t_i\}$.

The adsorption model is thus equivalent to a two-dimensional lattice gas with a grand canonical partition function Ξ , a many-body interaction energy $U(\{t_i\})$, and a chemical potential μ given as

$$e^{\beta\mu} = \lambda \rho_1^0(0) . \quad (9)$$

The fraction of sites of Λ which are occupied by spheres is given by^{1,5}

$$\theta = \frac{\lambda}{|\Lambda|} \frac{\partial}{\partial \lambda} \ln \Xi . \quad (10)$$

III. ADSORPTION OF LARGE SPHERES

If the hard sphere diameter σ slightly exceeds the lattice spacing d , then occupancy of two first-neighbor sites is excluded, and hence $U(\{t_i\})$ is infinite for all such excluded configurations. If $U(\{t_i\})$ is assumed to be zero for all allowed configurations, this is equivalent to assuming the pair correlation function is unity at distances greater than or equal to the second-neighbor separation, $\sqrt{3} d$, and that the n -body correlation functions are given by the Kirkwood superposition approximation⁶

$$g_n^0(\mathbf{R}_1, \dots, \mathbf{R}_n) = \prod_{\langle ij \rangle} g_2^0(\mathbf{R}_i, \mathbf{R}_j) . \quad (11)$$

Within the above approximations, the adsorption model is equivalent to the hard hexagon lattice gas, which has been solved exactly by Baxter.⁷ The isotherms for the adsorption model can then be computed using exact expressions for $\lambda \rho_1^0(0)$ as a function of θ which were obtained by Joyce⁸ for the equivalent hard hexagon lattice gas. We noticed that these expressions have a more compact form when $\lambda \rho_1^0(0)$ is written as a function of the variable

$$\phi = \theta(1 - \theta) . \quad (12)$$

The adsorption model undergoes an order-disorder transition at the fluid-solid interface at a critical coverage $\theta_c = (5 - \sqrt{5})/10 = 0.2764$, which corresponds to the value $\phi_c = 1/5$.

The exact expression for $\lambda \rho_1^0(0)$ as a function of ϕ in the disordered region, $\phi \leq 1/5$, can be written as

$$\lambda \rho_1^0(0) = Q[Q_0^2 Q_1^{1/2} + Q_2 - Q_0(2Q_3 + 2Q_2 Q_1^{1/2})^{1/2}] , \quad (13)$$

where

$$Q = (8\phi^6)^{-1}[1 - 5\phi + 5\phi^2 + (1 - 4\phi)^{1/2}(1 - 3\phi + \phi^2)]$$

$$Q_0 = 1 - 5\phi$$

$$Q_1 = (1 - \phi)(1 - 5\phi) \quad (14)$$

$$Q_2 = (1 - 4\phi)^{1/2}(1 - 11\phi + 33\phi^2 - 11\phi^3)$$

$$Q_3 = 1 - 16\phi + 90\phi^2 - 198\phi^3 + 119\phi^4 - 10\phi^5 .$$

The expression in the ordered region, $\phi \geq 1/5$, is given as

$$\lambda \rho_1^0(0) = \frac{-2 + 9\phi - 6\phi^2 - (2 - 5\phi)(1 - 4\phi)^{1/2}}{1 - 12\phi + 33\phi^2 + (5\phi - 1)^{3/2}(9\phi - 1)^{1/2}} . \quad (15)$$

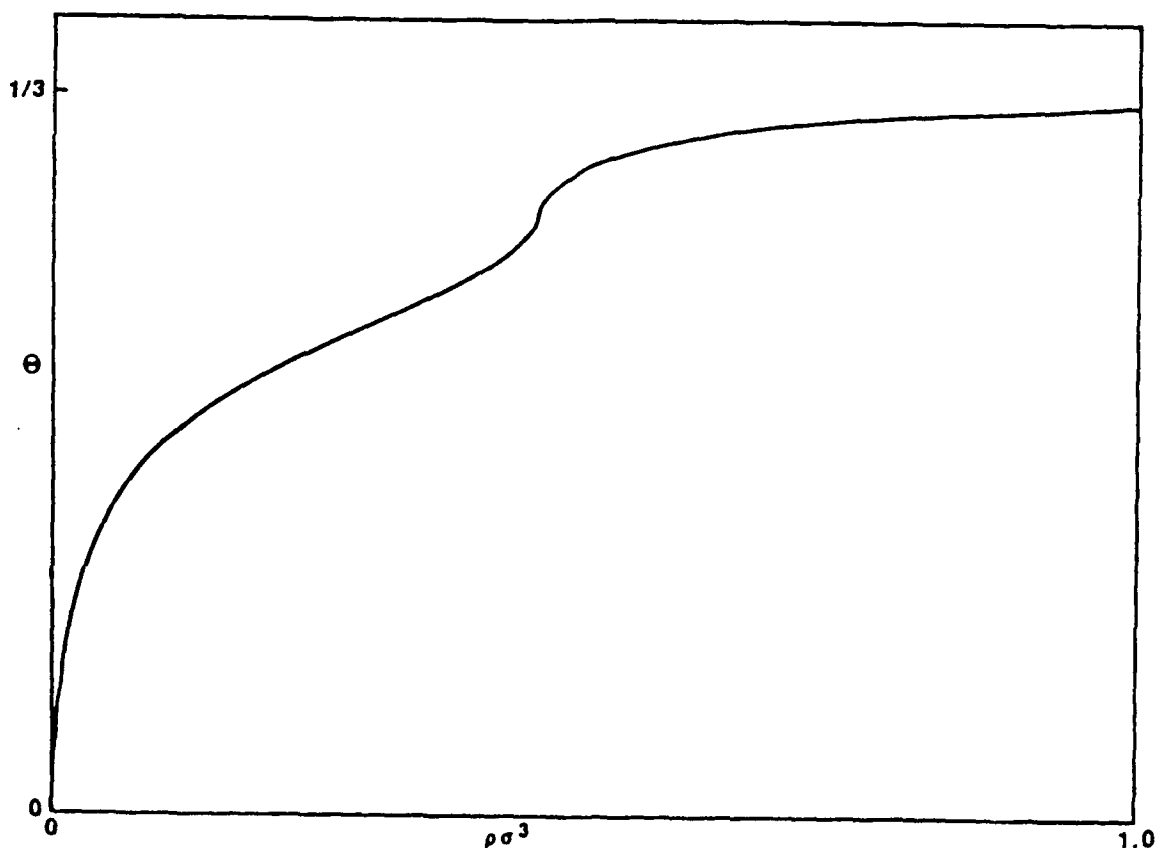


Figure 1. An isotherm with $\lambda/\sigma^3 = 10$ for the case $d < \sigma < \sqrt{3} d$.

At the transition, $[\lambda \rho_1^0(0)]_c = (11 + 5\sqrt{5})/2 = 11.09\dots$

The contact single particle density as approximated by the Percus-Yevick (PY) theory is^{9,10}

$$\rho_1^0(0)\sigma^3 = \frac{6\eta(1+2\eta)}{\pi(1-\eta)^2}, \quad (16)$$

where $\eta = (\pi/6)\rho\sigma^3$ is the packing fraction. The maximum density possible for hard spheres is $\rho\sigma^3 = \sqrt{2}$, which occurs at closest-packing.

Isotherms in the θ versus $\rho\sigma^3$ plane can be easily calculated using Eqs. (13) - (16). An isotherm with $\lambda/\sigma^3 = 10$ is illustrated in Fig. 1.¹

IV. ADSORPTION OF SMALL SPHERES

If the lattice spacing d greatly exceeds the hard sphere diameter σ , then the correlation functions can all be assumed to be unity for distances as large as d . This is equivalent to assuming $U((t_i))$ in Eq. (6) is zero for all allowed configurations, and Eq. (8) becomes²

$$\Xi = [1 + \lambda \rho_1^0(0)]^{|A|}. \quad (17)$$

Equations (10) and (17) then yield the Langmuir adsorption isotherm

$$\theta = \frac{\lambda \rho_1^0(0)}{1 + \lambda \rho_1^0(0)}. \quad (18)$$

The system in this case has no lateral interactions and does not undergo a phase transition.

For the case in which the lattice spacing is identical to or slightly exceeds the hard sphere diameter, if the pair correlation function is approximated to be unity for distances as large as the second-neighbor lattice spacing, and if the n-body correlation functions are approximated using the Kirkwood superposition approximation of Eq. (11), these approximations are equivalent to assuming that

$$U((t_i)) = W \sum_{nn} t_i t_j, \quad (19)$$

where W is the pair potential of mean force at the first-neighbor lattice spacing, i.e.,

$$e^{-\beta W} = g_2^0(d) . \quad (20)$$

The equivalent lattice gas thus has a partition function given by Eq. (8) and Eq. (19). A first-order phase transition occurs in this lattice gas on the triangular lattice if¹

$$\lambda \rho_1^0(0) = [g_2^0(d)]^{-3} . \quad (21)$$

The two-phase coexistence surface for this transition has been calculated exactly and is given by¹²

$$\theta = \frac{1}{2}(1 \pm [1 - 16g_2^0(d)[g_2^0(d) - 1]^{-3}[g_2^0(d) + 3]^{-1}]^{1/8}) . \quad (22)$$

The parameters at the critical point of this transition, which occurs at $\theta = 1/2$, are given from Eq. (21) and Eq. (22) as¹

$$[g_2^0(d)]_c = 3$$

$$[\lambda \rho_1^0(0)]_c = 1/27 . \quad (23)$$

For the special case $\sigma = d$, we let $g_2 = g_2^0(\sigma)$, and the PY approximation to the contact pair correlation function^{9,10}

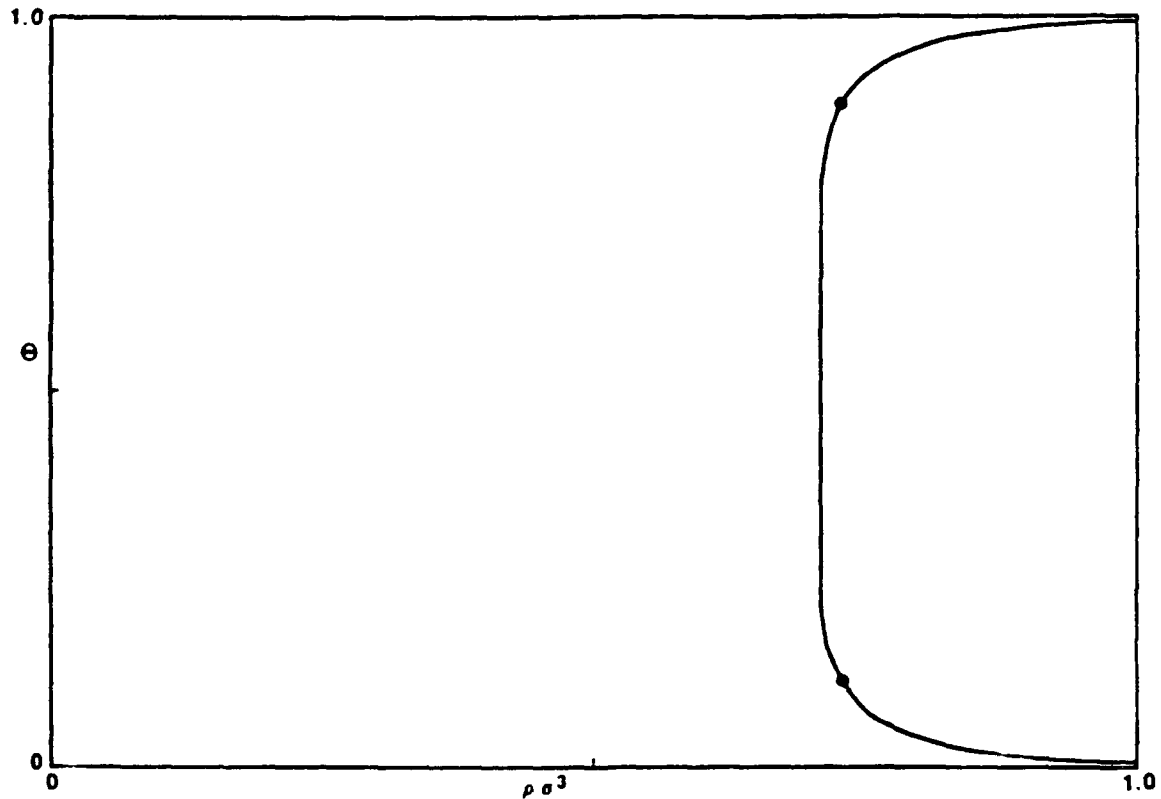


Figure 2. The coexistence curve for the case $\sigma = d$. The two coexisting phases on the isotherm with $\lambda/\sigma^3 = 0.01$ are marked with dots.

$$g_2 = \frac{1 + \eta/2}{(1 - \eta)^2} \quad (24)$$

can be used with Eq. (22) to plot the two-phase coexistence surface in the $(\theta, \rho\sigma^3)$ plane. For an appropriate fixed value of λ/σ^3 , the density at which a phase transition occurs on this isotherm can be calculated using Eqs. (16), (21), and (24).¹ For example, on the isotherm for which $\lambda/\sigma^3 = 0.01$, the two-phase coexistence occurs at $\rho\sigma^3 = 0.727$ with $\theta = 0.886$ and $\theta = 0.114$. These two transition points are pictured on the two-phase coexistence curve in Fig. 2.

Although the isotherms for this case have not been calculated exactly (this would be equivalent to solving the Ising model in non-zero field), many exact coefficients in series approximations to θ have been obtained. Letting $y = [\lambda\rho_1^0(0)g_2^3]^{-1}$, at low densities ($y > 1$)¹³

$$\theta_l(y) = \sum_{r=1}^{\infty} r y^{-r} c_r(g_2^{-1}) , \quad (25)$$

and at high densities ($y < 1$)

$$1 - \theta_h(y) = \sum_{r=1}^{\infty} r y^r c_r(g_2^{-1}) , \quad (26)$$

where c_r is a polynomial in g_2^{-1} . The hole-particle symmetry present in the lattice gas with first-neighbor interactions is exhibited in the relationship, where $y < 1$,

$$\theta_l(y^{-1}) = 1 - \theta_h(y) . \quad (27)$$

Equation (21) implies the first order transition occurs at $y = 1$.

We have constructed approximants² which are a natural extension of Langmuir's isotherm

$$\begin{aligned} \theta_l(y) &= \frac{P(y^{-1})}{1 + P(y^{-1})} \\ 1 - \theta_h(y) &= \frac{P(y)}{1 + P(y)} , \end{aligned} \quad (28)$$

where $P(y^{-1})$ can be written as

$$P(y^{-1}) = \sum_{r=1}^m p_r(g_2) [\lambda\rho_1^0(0)]^r . \quad (29)$$

The coefficients $p_r(g_2)$ are polynomials in g_2 which are determined by requiring

that the coefficients in the series expansions of Eq. (28) match the first m coefficients of Eq. (25) and Eq. (26). Written in terms of $f = g_2 - 1$, the polynomials $p_r(g_2)$, $r \leq 8$, for the triangular lattice were calculated to be

$$\begin{aligned}
 p_1 &= 1 \\
 p_2 &= 6f \\
 p_3 &= -6f + 45f^2 + 6f^3 \\
 p_4 &= 6f - 120f^2 + 344f^3 + 108f^4 + 12f^5 \\
 p_5 &= -6f + 225f^2 - 1680f^3 + 2478f^4 + 1374f^5 + 315f^6 + 30f^7 \\
 p_6 &= 6f - 360f^2 + 4920f^3 - 19788f^4 + 15474f^5 + 14640f^6 + 5298f^7 \\
 &\quad + 1008f^8 + 84f^9 \\
 p_7 &= -6f + 525f^2 - 11270f^3 + 82803f^4 - 205830f^5 + 66926f^6 + 135396f^7 \\
 &\quad + 71274f^8 + 20776f^9 + 3507f^{10} + 294f^{11} + 7f^{12} \\
 p_8 &= 6f - 720f^2 + 22224f^3 - 254568f^4 + 1179828f^5 - 1905384f^6 \\
 &\quad - 101754f^7 + 1068366f^8 + 817260f^9 + 330282f^{10} + 83868f^{11} \\
 &\quad + 13374f^{12} + 1224f^{13} + 48f^{14} .
 \end{aligned} \tag{30}$$

Using $\theta_l(y)$ and $\theta_h(y)$ of Eq. (28), together with a switching function $\eta(y)$ which vanishes at $y = 0$ and becomes unity as $y \rightarrow \infty$, a continuous approximation to θ which is accurate both at high and low fluid densities can be constructed as²

$$\theta(y) = \theta_l(y)\eta(y) + \theta_h(y)[1 - \eta(y)] . \tag{31}$$

Since $\theta_l(y)$ and $\theta_h(y)$ have the symmetry of Eq. (27), then if $\eta(y)$ satisfies $\eta(y^{-1}) = 1 - \eta(y)$, the approximation to θ given by Eq. (31) also satisfies $\theta(y^{-1}) = 1 - \theta(y)$. A possible choice for the switching function is

$$\eta(y) = \frac{1}{2}\{1 + \operatorname{erf}[s(y - y^{-1})]\} , \tag{32}$$

where s is a measure of the sharpness of the change between the two limiting values of $\eta(y)$.

V. EFFECTS OF THREE-BODY CORRELATIONS

Using pair correlations only, we can estimate the fluid density at the critical point of the first-order transition for the case $\sigma = d$ by combining the

condition $(g_2)_c = 3$ with the PY contact pair correlation function of Eq. (24). This yields the estimate¹

$$\rho_c \sigma^3 = \frac{13 - \sqrt{73}}{2\pi} = 0.7092 . \quad (33)$$

If the more accurate Carnahan-Starling (CS) pair correlation function^{10,11}

$$g_2 = \frac{1 - \eta/2}{(1 - \eta)^3} \quad (34)$$

is used for the calculation, the resulting estimate of this fluid density, $\rho_c \sigma^3 = 0.6678$, is slightly lower than that given by the PY correlation function.

A recent calculation by Attard and Stell¹⁵ using the Percus-Yevick 3 (PY3) theory,¹⁸ which includes three-body correlations, indicates that the Kirkwood superposition approximation of Eq. (11) is not accurate for the triplet correlation function of three spheres in mutual contact, but it is accurate for other possible configurations of three spheres on the triangle lattice.³

An improved estimate of $U(\{t_i\})$ is then given as³

$$U(\{t_i\}) = W \sum_{nn} t_i t_j + W_3 \sum_{\Delta} t_i t_j t_k , \quad (35)$$

where the second sum is over all triangles of nearest neighbor sites on the lattice. From Eq. (6) and Eq. (35), we can identify W as the pair potential of mean force and $W_3 + 3W$ as the potential of mean force for three spheres in mutual contact.

This is equivalent to the superposition approximation³

$$g_n^0(\mathbf{R}_1, \dots, \mathbf{R}_n) = \prod_{nn} g_2 \prod_{\Delta} g_3 / g_2^3 , \quad (36)$$

where g_3 is the triplet correlation function for three spheres in mutual contact, $g_2 = e^{-\beta W}$, and $g_3 / g_2^3 = e^{-\beta W_3}$.

Within this triplet correlation approximation, the model is equivalent to a lattice gas with pairwise interactions, W , and three-body interactions, W_3 .³ Using the interface method of Müller-Hartmann and Zittarz,¹⁷ the critical point of the coexistence surface in the lattice gas is predicted to satisfy,¹⁶ where $g_0 \equiv g_3 / g_2^2$,

$$(g_0)_c = 3 . \quad (37)$$

Using the PY3 theory,¹⁸ Attard and Stell¹⁵ calculated g_0 numerically over a wide range of fluid densities. We recently discovered³ that their numerical results are accurately approximated by the simple analytical expression

$$g_0 = \frac{4 - 7\eta + 7\eta^2 - 2\eta^3}{4(1 - \eta)^3} . \quad (38)$$

Using Eq. (37) and Eq. (38), the fluid density at the critical point of the transition is calculated to be $\rho_c \sigma^3 = 0.8409$.³ This estimate of the minimum fluid density necessary for a phase transition to occur at the fluid-solid interface is much larger than that predicted using only the pair correlation function and the Kirkwood superposition approximation.¹ The inclusion of triplet correlations is thus important for studying adsorption in this case of the model.

ACKNOWLEDGMENTS

D.H. was supported by the Robert A. Welch Foundation, grant P-0446. L.B. was supported by the Office of Naval Research and by EPSCoR EHR-910-8775.

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